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OBSERVATIONS ON THE EFFECTS OF SHEAR AND RELAXATION  
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MD DEPT OF CHEMICAL ENGINEERING. A K MCCLELLAN ET AL.

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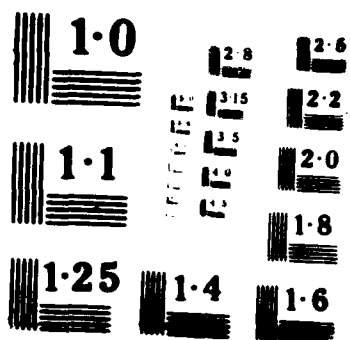
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Times on the Phase Behavior of Polymer Solutions

by

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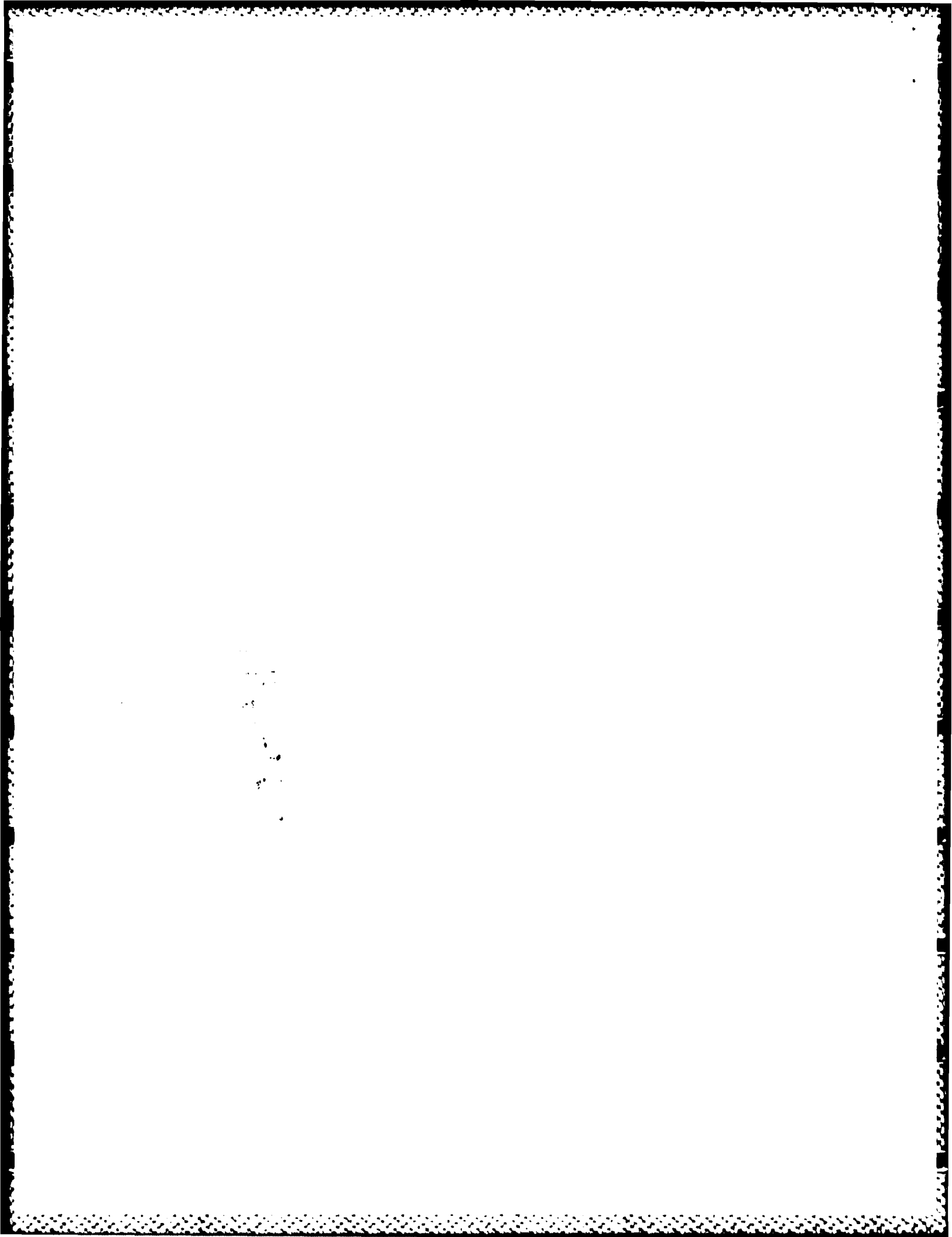
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## Observations on the Effects of Shear and Relaxation Times on the Phase Behavior of Polymer Solutions

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### ABSTRACT

Shearing (e.g., mixing) a polymer solution can shift the location of the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST) curves in pressure-temperature (P-T) space. Also, the location of these curves in P-T space is affected by the rate at which transition points are determined. Preliminary observations on the effects of shear and relaxation times on the phase behavior of the polystyrene-toluene-ethane system are presented.

### INTRODUCTION

In the course of determining the high-pressure phase behavior of the polystyrene (PS)-toluene-ethane system, we observed some unusual behavior associated with the rate at which the solution was mixed (i.e., sheared) and the rate at which cloud points were determined. The primary focus of the phase-behavior studies was to determine the effect of ethane, a variable-strength antisolvent, on the location of the lower-critical-solution temperature (LCST) and the upper-critical-solution temperature (UCST) curves of the PS-toluene system (McClellan et al., 1985; McClellan et al., 1986). Sacki et al. (1973) have shown that the LCST curve for the PS-toluene system begins at 284°C for PS with a weight average molecular weight of 150,000. Figure 1 shows that the LCST curve (i.e., the liquid → liquid + liquid curve) for the PS-toluene system can be shifted to quite

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moderate temperatures with the addition of ethane to the mixture (McClellan et al., 1986).

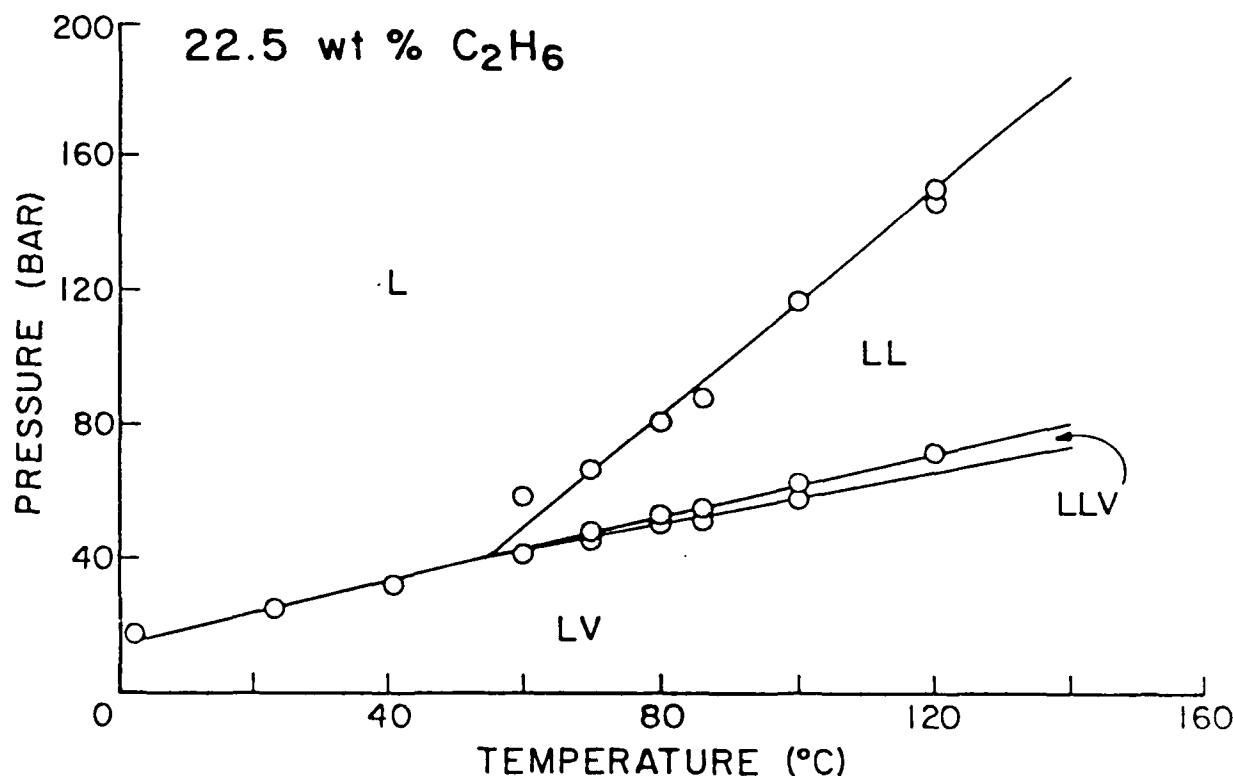


Fig. 1. Phase behavior for a 4.1 wt-% polystyrene - 79.4 wt-% toluene - 22.5 wt-% ethane mixture. The liquid  $\rightarrow$  liquid+liquid transition curve is termed the LCST curve.

Although Saeki et al. (1973) showed that the UCST for the PS-toluene system does not appear at temperatures above  $-70^{\circ}\text{C}$ , it is possible to shift the UCST curve to high-enough temperatures with the addition of ethane so that it eventually merges with the LCST curve. Figure 2 shows schematically how the addition of a light gas, or a supercritical fluid, affects the phase diagram for polymer solutions. The focus of this communication is to report our observations on the effect of mixing and polymer entanglement/disentanglement relaxation times on the location of the LCST and UCST phase-border curves.

#### SHEAR EFFECTS

The LCST and UCST phase-border curves were measured using a high-pressure, variable-volume cell which allows for visual observations of the phases (McHugh and Guckes, 1985). As shown in Table 1, we found that the pressure of the system was dependent on whether or not the PS-toluene-ethane solution was being mixed. When the solution was stirred (i.e., changing from a quiescent to a sheared state), the system pressure increased when operating in the two-phase,



liquid-liquid region of the phase diagram, yet it decreased when operating in the single-phase, liquid region. These pressure changes are very reproducible.

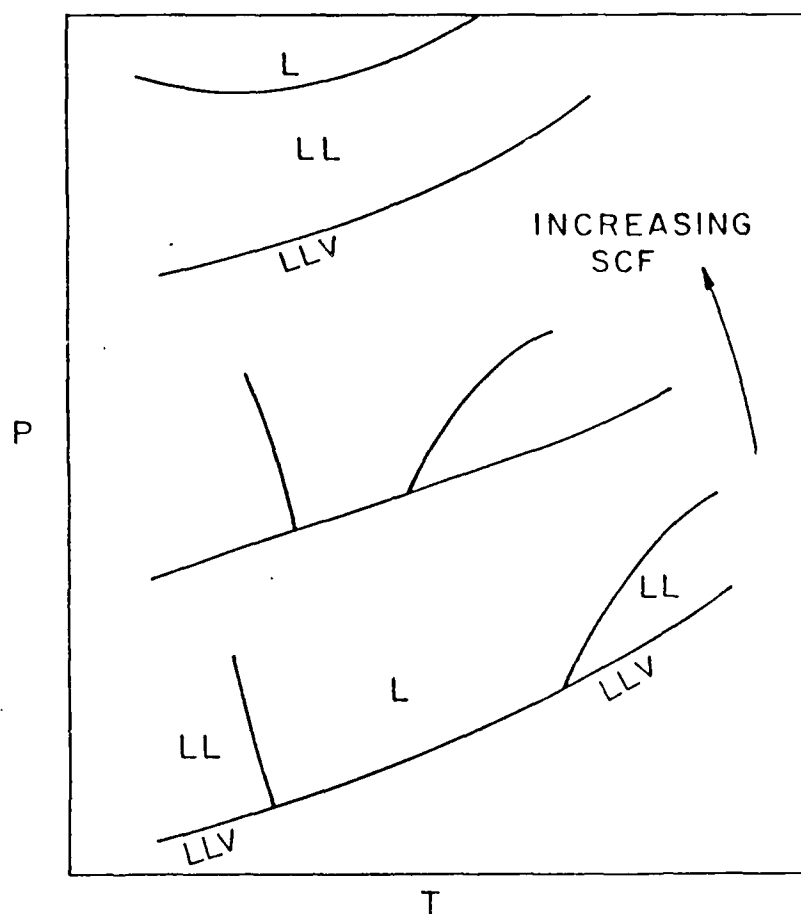


Fig. 2. Effect a supercritical fluid (SCF) on the phase diagrams of polymer solutions. Note that the two liquid  $\rightarrow$  liquid+liquid transition curves (i.e., the UCST and LCST curves) merge when high concentrations of the SCF are added to the polymer solution.

The change in pressure with and without stirring is associated with changes in the specific volume of the system. With stirring, PS molecules will configure in a more extended conformation and will expose more surface area to the solvent as compared to the coiled configuration occupied by PS molecules in an unstirred, quiescent environment. Therefore, the volume occupied by the polymer-solvent mixture depends on the specific interactions between the polymer and solvent (Tirrell, 1986). If the polymer and solvent "like each other", the volume of the mixture decreases when it is mixed and the system pressure also decreases. This effect is observed in the single-phase, liquid region of Figure 1 since, at elevated pressures and/or at moderate temperatures, the toluene-ethane mixture is a good solvent for polystyrene. With a poor polymer solvent, the volume of the mixture will increase when it is mixed and, hence, the system pressure should also increase in a

TABLE 1.

Effect of mixing on the system pressure. For these mixtures the concentration of polystyrene in toluene (on an ethane-free basis) remains fixed at 5.0 wt-%.

wt-% C <sub>2</sub> H <sub>6</sub> in solution	Temperature (°C)	Pressure without stirring (bar)	Phases present	Pressure change with stirring (bar)
22.5	130.0	74.5	LL	+ 1.03
22.5	88.5	100.0	LL	+ 0.34
22.6	69.9	66.2	LL	0.00
24.9	70.0	151.7	L	-0.21
25.4	70.0	179.3	L	0.41
22.6	69.9	72.4	L	0.00
22.5	45.0	36.5	L	0.00

closed system. This effect is observed in the liquid-liquid region of Figure 1 since the toluene-ethane mixture has become such a poor quality solvent that it no longer can dissolve the polystyrene. The magnitude of the pressure change associated with mixing is sensitive to the system temperature, the quality of the solvent (in our case the quality is controlled by the amount of ethane in the solution), and the molecular weight of the polymer - - the higher the molecular weight the larger the shear effect (in our studies the weight average molecular weight is only 150,000) (Wolf and Jend, 1979; Kramer and Wolf, 1985).

If the solvent is exceptionally poor, as is the case when a large amount of ethane is added to the PS-toluene solution, it is possible for the polystyrene to form solid particles with mixing. For a mixture with 3.6 wt-% PS, 67.4 wt-% toluene, and 29.0 wt-% ethane, solid particles of polystyrene were observed in the two-phase, liquid-liquid region when the system was vigorously mixed. It should be noted that the polymer-rich liquid in this situation is very viscous and gel-like in appearance indicating that very little toluene-ethane solvent is present in this phase. When the mixing was stopped, the solid particles settled on the top of the polymer-rich phase and slowly melted or dissolved. If stirring was resumed the solid particles quickly reformed. With stirring the solid phase was also present during cloud-point determinations. Rangel-Nafaile et al., (1984) note that numerous authors have also observed the formation of polymer particles for certain polymer solutions which were subjected to mild deformations.

The ability to form solid polystyrene particles can be interpreted by reexamining the role of ethane. As mentioned previously, ethane acts as a variable-strength antisolvent - - variable-strength since the solvent power of ethane increases considerably as it is compressed (McHugh and Krukonis, 1986). As ethane is added to the mixture the LCST is shifted to lower temperatures, the UCST curve is shifted to higher temperatures, and the three-phase, solid-liquid-liquid (SLL) curve is also shifted to higher temperatures. Figure 3 shows schematically how solidification phenomena can occur at high ethane concentrations for PS-toluene-ethane mixtures. Superimposed on the

effect of ethane is the effect of a shear field (i.e., mixing). With mixing the SLL curve should be shifted to even higher temperatures since the polystyrene molecules are being aligned and are therefore more likely to solidify (Vrahopoulo-Gilbert and McHugh, 1984). The occurrence of this solid phase over wide ranges of P-T space is a consequence of the multicomponent nature of polymer solutions. The SLL curve is actually an SLL area in the same manner that the LLV curve in Figure 1 is an LLV area (McClellan et al. 1985; McClellan et al., 1986). Unfortunately, we are unable to characterize the flow pattern experienced by the solution due to the geometry of the experimental apparatus used for obtaining phase-behavior information.

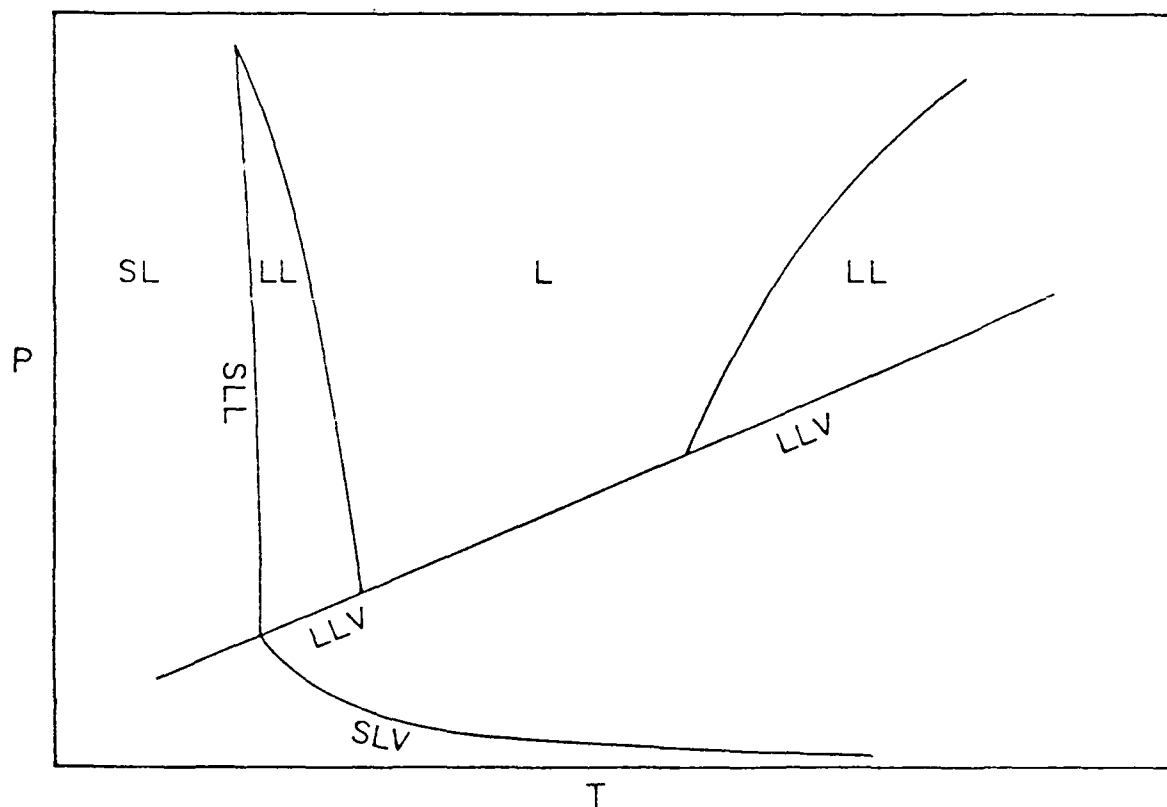


Fig. 3. Schematic phase diagram for a polystyrene-toluene-ethane mixture at high concentrations of ethane.

#### RELAXATION EFFECTS

The rate at which the LCST transitions were measured in this study was an important variable in reproducing the transition. The PS-toluene-ethane solution is isothermally decompressed at a very slow rate to obtain a cloud-point pressure (i.e., an LCST point). If the solution is quickly repressurized back into the one-phase region and again slowly decompressed, a different cloud-point pressure is observed. These cloud-point pressures were found to vary by as much as 7 bar depending on the length of time the solution remained in the one-phase region prior to determining the cloud-point.

This hysteresis in cloud-point pressure is a consequence of the entanglement of the polymer molecules and the time it takes for disentanglement (Laufer et al., 1973; Peterlin, et al., 1965). The degree of entanglement is expected to be very different in the liquid-liquid region as compared to the single-phase region, since the PS concentration in the polymer-rich phase in the two-phase region is about 20 to 25 wt-% while in the single-phase region it is less than 5 wt-%. A finite time is necessary for polystyrene molecules to disentangle or to entangle in solution, hence, spurious LCST transitions will be obtained if sufficient time is not allowed for these processes to occur.

## CONCLUSIONS

The observations discussed in this communication indicate that the normal methods used for obtaining the phase behavior of mixtures may not result in equilibrium data when applied to polymer solutions. The process of mixing, which normally is associated with reducing the time for a solution to reach equilibrium, can drive a polymer mixture away from an equilibrium state. Mixing a polymer solution changes the system's entropy and enthalpy which in turn affects the location of phase-boundary curves. Also, sufficient time must also be allowed for the polymer to relax in solution. More work is needed to quantify these effects on the phase diagrams of polymer solutions.

## ACKNOWLEDGEMENTS

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